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Union Carbide Corporation

FLUORINE OXIDIZERS

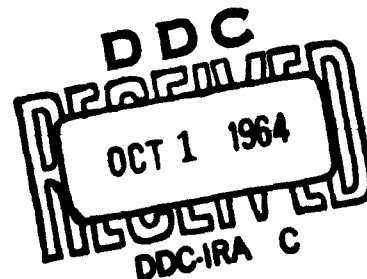Quarterly Technical Summary Report No. 5

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I. ABSTRACT

Chloryl fluoride reacts with cesium fluoride at 0-25° to produce a solid having a limiting composition near "CsF_2". The solid, however, possesses little oxidizing strength. Reaction of chloryl fluoride with cesium oxide gives a solid product containing cesium, fluorine and chlorine in variable composition. These experiments gave no evidence indicating the formation of a stable fluorochlorate salt, Cs_2ClO_3F, or of a difluorochlorate salt, $CsClO_2F_2$.

Chloryl fluoride and chlorine trifluoride react with cesium azide with formation of fluorine-containing solids. These reactions are being studied as possible routes to fluorine-nitrogen anions.

The reaction of potassium perchlorate with bromine trifluoride gives nearly quantitative yields of chloryl fluoride and only minor amounts of perchloryl fluoride.

Platinum hexafluoride and chlorine trifluoride react to form chlorine pentafluoride and the solid compound $ClF_3 \cdot PtF_5$. Thermal decomposition of this substance produces fluorine, chlorine trifluoride and platinum tetrafluoride.

II. INTRODUCTION

Work during this quarter has been aimed principally at elucidating the chemical properties of chloryl fluoride and of platinum hexafluoride. The initial effort with chloryl fluoride has been a study of chemical reactions which might lead to formation of fluorochlorate ions or provide evidence concerning the stability of such ions. The reactions chosen were those between chloryl fluoride and alkali metal fluorides and oxides, viz., CsF and Cs_2O, which could provide routes to cesium difluorochlorate, $CsClO_2F_2$, and to cesium fluorochlorate, Cs_2ClO_3F, respectively. As part of our overall objectives of investigating the chemistry of chloryl fluoride and of synthesizing new, solid oxidizers, the reaction of chloryl fluoride with cesium azide has been investigated as a possible route to nitrogen-fluorine anions. Preliminary results also are reported of a study of the related reaction between chlorine trifluoride and cesium azide.

Platinum hexafluoride has been shown to be a very powerful oxidizing agent as evidenced by its ability to oxidize molecular oxygen[1] to O_2^+ PtF_6^{-1} and xenon[2] to Xe^+ PtF_6^{-1}. This great oxidizing strength of platinum hexafluoride suggests its utility as a reagent for synthesis of other highly oxidized species. Our program is directed towards a broad investigation into the reactions of PtF_6 with various fluorine compounds. During this quarter the reaction between platinum hexafluoride and chlorine trifluoride has been investigated in detail.

One further aspect of this quarter's work carries over from our previous study of bromine trifluoride as an electrolytic solvent. This has been a study of the reaction between potassium perchlorate and bromine trifluoride, the detailed stoichiometry of which is herein reported.

III. RESULTS AND DISCUSSION

Reaction of Chloryl Fluoride with Cesium Fluoride

The reaction of chloryl fluoride with cesium fluoride was studied as a possible route to $CsClO_2F_2$. Stoichiometric data obtained from eleven experiments are summarized in Table I. As can be seen, a wide scatter of results was obtained for the chloryl fluoride to cesium fluoride reacting ratio, with values for this ratio ranging from 0.31 to 1.04. With but one exception (Exp. No. 1) the reaction was found to produce only minor amounts of oxygen. Regardless of the observed reacting ratio and other reaction variables, however, the weight gain of the solid reactants was fairly constant at about 17%. Based on the total weight of solid product obtained and the number of mmoles of cesium fluoride taken for reactions, the average molecular weight of the products was calculated as 179 ± 5.

The non-volatile reaction product is a white to pale yellow solid which fumes and deliquesces in air. When added to water, the solid reacts with moderate vigor and apparent evolution of a gas with a pungent fluorine-compound odor. Similar behavior was noted when the hydrolysis was carried out on the vacuum line but no gases volatile at -78° were produced, thus showing the absence of F_2, OF_2 or O_2. Essentially the same results were obtained when hydrolysis was carried out in acid or alkaline solution. Solutions of the substance always possessed sufficient oxidizing strength to colorize acid iodide solution but quantitative analysis showed that not more than a trace of oxidant was present.

In a capillary tube, the solid product melted over the range 130 to 150° to an opaque, viscous fluid which was stable at 300°. When

heated strongly with a flame in a quartz tube, the material either boiled

or evolved gases and then solidified. However, only trace amounts of gases

were found after cooling the quartz tube to 25°. The x-ray diffraction

pattern (Table II) of the substance appeared unique except possibly for a

poorly defined cesium fluoride phase. An infrared spectrum of the substance,

obtained on a pressed KBr disc, showed broad bands centered at 3.0, 4.85,

5.45, 6.8, 8.15, 10.5 and 12.5μ. The results of numerous elemental analyses

of the product are shown in Table I. In general, the highest fluorine

results were obtained when the samples were hydrolysed in closed systems

or on the vacuum line. The lower results, obtained on samples hydrolysed

in open containers, suggest loss of volatile fluorine-containing materials.

The solid product obtained from Exp. 6 was treated directly with

excess BF_3 in an effort to liberate $ClO_2F \cdot BF_3$. The total amount of BF_3

absorbed corresponded very closely to the sum of CsF taken and ClO_2F

consumed but no $ClO_2F \cdot BF_3$ was formed; only a small amount of ClO_2

was obtained. The weight of the solid product was very close to

that expected for total conversion to $CsBF_4$ and this identity was

confirmed by the x-ray pattern.

Although the wide scatter of results obtained prohibit definitive

interpretation, it does seem clear that no stable cesium difluoro-chlorate

compound forms in this system. Beyond that deduction only a few trends may

be noted. There is a definite and fairly constant weight increase of the

solid reactant due to the reaction. The analyses indicate that this weight

increase is principally due to an increased fluorine content, and that the

limiting F/Cs ratio is 2. This excess fluorine content cannot be accounted

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for in terms of $CsClO_2F_2$, $CsClF_4$, or other fluorochlorate species, since the determined chlorine content (as ClO_4^-, ClO_3^-, ClO_2^-, ClO^- and Cl^-) is inadequately low. It is probable, however, that the solid contains oxygen in the form of an oxyanion of chlorine and this could account partially for the low total analytical figures. If it is assumed that the fluorine analyses are low for those samples hydrolysed in open systems, then the analytical results suggest a limiting composition of CsF_2 for the solid reaction product. The lack of significant oxidizing strength of the material is difficult to reconcile with such a formulation.

Reaction of Chloryl Fluoride with Cesium Oxide.

The reaction of chloryl fluoride with cesium oxide occurs rapidly at temperatures of -78° or lower with evolution of oxygen and chlorine. Stoichiometric data obtained for the reaction are summarized in Table III (Exps. 1 through 4). The molar ratio of chloryl fluoride consumed to cesium oxide taken varied from 1.07 to 2.39 for four experiments, whereas the molar ratio of oxygen evolved to chloryl fluoride consumed was close to unity. Approximately two-thirds of the chlorine content of the chloryl fluoride entering reaction was liberated as elemental chlorine. The solid, non-volatile product contained cesium, chlorine and fluorine but the composition was variable, and no formulation such as that of the fluorochlorate salt could be deduced.

During two of the experiments (Exps. 5 and 6, Table III), the reaction of chloryl fluoride with cesium oxide occurred as a rapid, luminescent reaction. This phenomenon, which occurred as the reaction mixtures were being warmed from -196° to -78°, appeared as a flash of bright, white light of a few seconds duration. It was readily visible through the walls of the

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Kel-F reactor and seemed to occur at temperatures close to -78° but was
not accompanied by pressure damage to the reactor. Examination of the
volatile reaction products showed that all of the chloryl fluoride had
been consumed with liberation of one mole of oxygen per mole of chloryl
fluoride. The only other volatile product was chlorotrifluoromethane,
which must have resulted from attack of the reactants, or reaction
intermediates, on the Kel-F reactor. The solid reaction products were
found to contain cesium, fluorine and chlorine in non-stiochiometric ratios.

In summary, the reaction of chloryl fluoride with cesium oxide
was found to be unpredictable and gave solid products of varying composition.
The luminescent reaction was originally observed during our second attempt
to carry out the reaction of cesium oxide with chloryl fluoride. The
succeeding experiments were carried out in an effort to reproduce consistently
this result, but the luminescent reaction occured in only one other experiment.
No evidence suggestive of special conditions or catalysts necessary for
initiating this reaction was obtained.

The fast rate of the luminescent reaction and the fact that one
mole of oxygen evolves per mole of chloryl fluoride suggests that the
overall reaction may simply be decomposition into O_2 and ClF. Subsequent
reaction of ClF with the solid reactant could then account for the
composition of the non-volatile product.

Reaction of Chloryl Fluoride and Chlorine Trifluoride with Cesium Azide.

The reaction of chloryl fluoride with cesium azide takes place
vigorously at 25° but smoothly at -78°. The reaction proceeds in a 1:1
reacting ratio with evolution of one mole each of nitrogen and oxygen
per mole of chloryl fluoride taken. The stoichiometric data, therefore,

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may be summarized by the equation:

$$CsN_3 + ClO_2F \longrightarrow O_2 + N_2 + CsNClF \text{ (by difference)}.$$
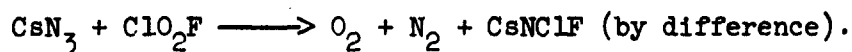
Analysis of the non-volatile reaction product gave the ratio $Cs/F/Cl = 1.0/0.49/0.63$; the nitrogen analysis has not yet been obtained. The white, solid product did not melt below 300°. An x-ray diffraction pattern showed a clearly defined CsCl phase but no other crystalline phase. Infrared bands at 3.0, 4.75, 6.55, 7.22, 7.97, 8.34, 8.90 and 10.3μ were observed on a KBr disc of the material. A concentrated solution of the solid in water was deep yellow in color but on dilution the color faded completely. These aqueous solutions possessed no oxidizing strength towards acid iodide solution.

The reaction of chlorine trifluoride with cesium azide also takes place smoothly at -78° with liberation of one mole of nitrogen per mole of cesium azide taken. Chlorine and possibly chlorine monofluoride were also produced in the reaction. The solid residue was found to contain cesium, fluorine and chlorine in the ratio $Cs/F/Cl = 1.0/1.56/.11$ and a nitrogen content by difference of 4.86%.

These results on the reactions of chloryl fluoride and chlorine trifluoride with cesium azide require verification and refinement. Nevertheless, the results indicate that the solid products contain nitrogen and fluorine, possibly in the form of a nitrogen-fluorine anion.

Reaction of Potassium Perchlorate with Bromine Trifluoride.

The reaction of potassium perchlorate with bromine trifluoride takes place slowly at 25° with liberation of oxygen, bromine, chloryl fluoride and minor amounts of perchloryl fluoride. The principal reaction may be represented by the equation:

$$3KClO_4 + 5BrF_3 \longrightarrow 3O_2 + Br_2 + 3KBrF_4 + 3ClO_2F.$$
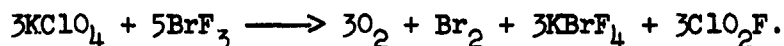
Our early interpretation of the reaction as leading to the formation of stable fluorochlorate species in solution must be withdrawn since experimental data has been obtained which nicely confirms the stoichiometry of the above equation. Nevertheless, it has been observed that when the reacting ratio of $KClO_4$ to BrF_3 is large, i.e., when the solution is concentrated, the reaction proceeds beyond the 50% completion stage only very slowly. The reasons for this behavior are not clear.

Reaction of Platinum Hexafluoride with Chlorine Trifluoride

Platinum hexafluoride reacts with chlorine trifluoride with formation of chlorine pentafluoride and the compound $PtF_5 \cdot ClF_3$. Data for the reaction, shown in Table IV, are best interpreted in terms of the equation:

$$2/3PtF_6 + ClF_3 \longrightarrow 2/3PtF_5 \cdot ClF_3 + 1/3ClF_5.$$
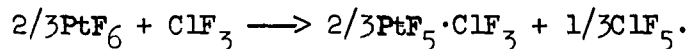
For the first five experiments shown in Table IV, the yields of $PtF_5 \cdot ClF_3$ and ClF_5 were somewhat greater than required by the above equation. Since the reacting ratio chosen for these experiments was $PtF_6 : ClF_3 = 1:1$, it is thought that some further reaction between PtF_6 and the adduct $PtF_5 \cdot ClF_3$ must also occur. When the reacting ratio of $PtF_6 : ClF_3$ was 2:3 (Exps. 6 and 7) the yields of $PtF_5 \cdot ClF_3$ and ClF_5 were very close to those required by the proposed equation. Furthermore, when an excess of chlorine trifluoride was used, all of the platinum hexafluoride was converted to the adduct.

The compound $PtF_5 \cdot ClF_3$ is a bright yellow solid which reacts violently with water to produce foul-smelling gases. In these respects, the compound appears identical to that obtained by Bartlett[3] from

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PtF_5 and ClF_3, although our material appears to decompose rather than melt at 170° as did the compound described by Bartlett.

Thermal decomposition of $PtF_5 \cdot ClF_3$ at temperatures up to 620°C gives platinum tetrafluoride, chlorine trifluoride and fluorine. The experimental data, shown in Table V, are adequately described by the equation:

$$ClF_3 \cdot PtF_5 \longrightarrow PtF_4 + ClF_3 + 1/2F_2.$$
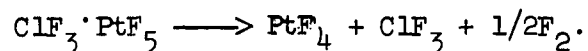
The validity of this equation is based on four experiments, which involved measurement of the quantities of ClF_3 and F_2 evolved, and of the changes in weight of the solid reactants, during decomposition. Platinum tetra-fluoride was identified through its x-ray diffraction pattern and by chemical analysis.
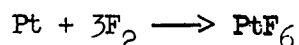
IV. EXPERIMENTAL

Apparatus

High vacuum systems, constructed from nickel tubing and traps, monel fittings and storage bulbs, Hoke TM440 valves, and Helicoid Monel Compound Gauges, are now in use. All reactions were carried out either in nickel or Kel-F reactors.

Chemicals

Platinum Hexafluoride was prepared by the reaction

$$Pt + 3F_2 \longrightarrow PtF_6$$

using the procedure described by Weinstock, Malm and Weaver.[4] Generally from 7 to 15 grams of PtF_6 were prepared in each run, purified, and stored in a monel flask on the vacuum system.

Chloryl fluoride was prepared from bromine trifluoride and potassium chlorate as described by Woolf.[5] It was purified by trap to trap fractionation until vapor pressure measurements agreed with those reported in the literature.[6] Storage in a monel bulb at 25° was satisfactory although slow decomposition occurs with formation of non-condensable gas.

Chlorine trifluoride (Matheson Co.) was purified by repeated trap to trap distillation until vapor pressure measurements indicated a high state of purity.[7]

Cesium fluoride and cesium azide were obtained from K&K Labs., Inc. For a few experiments cesium fluoride was converted to the bifluoride which was then decomposed at 500°. Cesium fluoride prepared in this manner gave essentially the same results in the chloryl fluoride experiments as did the untreated compound. Cesium oxide was obtained from the Rare Metals Chemical Co. Analysis of this material for cesium and alkalinity indicated 95% purity as Cs_2O.

Reaction of Chloryl Fluoride with Cesium Fluoride. These reactions
were carried out in nickel or Kel-F reactors of 8-20 cc volume. The cesium
salt was transferred to the reactor inside of a dry box, and then thoroughly
pumped out on the vacuum line. Four-to-five-fold excesses of chloryl fluoride
were taken for reaction in order to insure the presence of some liquid
phase in the reactor. The pressures recorded in Table I are the estimated
vapor pressures of chloryl fluoride at the temperatures of the reactions.

Attempts were made to follow changes in the composition of the
gaseous reactants by infrared spectroscopy but no bands other than those
attributable to chloryl fluoride were detected. However, the spectrum of
chlorine dioxide coincides with part of the spectrum of chloryl fluoride,
so that the formation of ClO_2 could have gone undetected in the presence
of the large excess of chloryl fluoride. The gases recovered from the
reactions always contained materials more volatile than chloryl fluoride as
was shown by an increase in vapor pressure from 9 mm (before reaction)
to 20-40 mm (after reaction). Attempts to separate these substances by
fractionation were unsuccessful.

The solid products were analysed for cesium by precipitation as
the hexachloroplatinate (IV), for fluorine by thorium nitrate titration,
and for chlorine by the Volhard method. Aqueous solutions of the CsF-
ClO_2F products gave negative tests for ClO_4^- by precipitation with nitron.
All other oxidation states of chlorine were included in the analysis by
reduction to chloride with SO_2.

Reaction of Chloryl Fluoride with Cesium Oxide. The oxide was carefully
pulverized and loaded into the Kel-F reactors inside of a dry box. After
evacuation, chloryl fluoride was condensed into the reactor at -196°.

The molar ratio of chloryl fluoride to cesium oxide taken was between two and three in all experiments. Excess chloryl fluoride was recovered only from those experiments carried out at -78°.

The reaction gases were fractionated and identified by vapor pressure measurements. Chlorine was further identified by vapor density measurements, and the identity of chlorotrifluoromethane was confirmed by the infrared spectrum.

Reaction of Chloryl Fluoride with Cesium Azide. Chloryl fluoride, 2.37 mmoles, was condensed at -196° into a Kel-F tube containing 3.03 mmoles of CsN_3. The reactor was kept at -78° for 18 hours, after which time 4.73 mmoles of non-condensable gas and a trace of condensable gas were recovered. Analysis by VPC using a molecular sieve column showed the non-condensable gas to contain 2.23 mmoles of O_2 and 2.50 mmoles of N_2; hence the ratios were $O_2/ClO_2F = 0.94$ and $N_2/ClO_2F = 1.05$. No additional gases were evolved after heating the reactor to 100° for 30 minutes.

The white solid residue did not melt below 300°. Analysis gave 75.7% Cs, 5.36% F, and 12.58% Cl which defines the ratios Cs:F:Cl = 1.0: 0.49:0.63. The x-ray pattern showed a clearly defined CsCl phase with no unassigned lines. Bands at 3.0, 4.75, 6.55, 7.22, 7.97, 8.34, 8.90 and 10.3μ were observed in the infrared spectrum of the solid in a KBr disc.

Reaction of Chlorine Trifluoride with Cesium Azide. In a similar manner, the reaction of 2.48 mmoles of CsN_3 with 1.49 mmoles of ClF_3 for 5 hours at -78° produced 2.43 mmoles of N_2 and 0.43 mmoles of Cl_2. Analysis of the white, solid residue gave 76.1% Cs, 16.9% F and 2.16% Cl: Cs:F:Cl = 1.0:1.5:0.11.

Reaction of Potassium Perchlorate with Bromine Trifluoride. Reaction of 2.94 mmoles of $KClO_4$ with 2 ml of BrF_3 for 18 hours at 25° produced 3.23 mmoles of O_2, 0.15 mmoles of ClO_3F, 2.85 mmoles of ClO_2F and 0.81 mmoles of Br_2. The observed ratios are: $O_2/KClO_4 = 1.10$; $ClO_2F/KClO_4 = 0.97$; and $Br_2/KClO_4 = 0.28$; which define the equation

$$3KClO_4 + 5BrF_3 \longrightarrow 3KBrF_4 + 3ClO_2F + 3O_2 + Br_2.$$

The identity of the solid residue remaining after evaporation of the excess BrF_3 was confirmed by x-ray analysis as $KBrF_4$.

Reaction of Chlorine Trifluoride with Platinum Hexafluoride.

In a typical experiment, 3.39 mmoles of PtF_6 and 3.39 mmoles of purified ClF_3 were condensed into a nickel reactor equipped with a Hoke TM440 valve. The reactor was allowed to warm up slowly from -195°C to room temperature and remain overnight at this temperature. The reactor was then opened and the quantity of gaseous products measured. The gaseous products were fractionated using a -126°C trap. The material left in the -126°C trap was identified as ClF_5 by its infrared spectrum[8] and by vapor pressure measurements.

The bright yellow solid product was weighed and analyzed for platinum by reduction with hydrogen in a nickel boat. The average of three determinations gave 51.45% ($ClF_3 \cdot PtF_5$ requires 50.99% Pt). The adduct is very hygroscopic and difficult to handle. It reacts violently with water. The reduction in hydrogen can be facilitated by adding CCl_4 to the solid after weighing, and purging the reduction chamber with N_2 to eliminate the pressure of O_2 before passing H_2 into the system. This procedure eliminates the explosion which otherwise occurs. The temperature of the reduction tube was slowly increased from room temperature to 700°C. After reduction was completed the material was weighed as platinum metal.

The Thermal Decomposition of $ClF_3 \cdot PtF_5$

Weighed samples of $ClF_3 \cdot PtF_5$ were thermally decomposed in a nickel reactor. Decomposition begins at approximately 110°C. The temperature was increased to as high as 640°C where decomposition appeared to be complete. After cooling, the pressure of condensable and non-condensable gases were measured in standard volumes of the vacuum system. The F_2 produced in the reaction was absorbed by reaction with Hg and the amount of F_2 present determined by difference from the measurement of the total number of mmoles before and after absorption.[9] ClF_3 was kept behind in the system by a -196°C trap. ClF_3 was identified by infrared spectroscopy and vapor pressure measurements of the gas.

The PtF_4 was identified by x-ray diffraction analysis (comparison with Bartlett's pattern[3]) and by chemical analysis for Pt (found 71.12% Pt, theoretical for PtF_4:71.96%).

V. FUTURE WORK

Major effort will be directed towards continuing study of the
reactions of platinum hexafluoride with oxidized systems. The reactions of
cesium azide with chloryl fluoride and chlorine trifluoride will be investi-
gated in more detail in order to determine whether fluorine-nitrogen anions
are formed.

Because of the complexity of the cesium oxide-chloryl fluoride
reaction, it does not appear fruitful to contine this study. It would
be of interest, however, to define the conditions necessary for producing
the chemiluminescent reaction, and subsequently to examine the system
spectroscopically. No further effort is planned for the chloryl fluoride-
cesium fluoride reaction.

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TABLE I

Data for CsF-ClO$_2$F Reaction

Exp. No.	CsF taken mmoles	ClO$_2$F consumed mmoles	$\frac{ClO_2F}{CsF}$	reaction temperature °C	time of reaction hrs.	pressure in reactor atm.	O$_2$ obtained mmoles	Ave. M.W. of product per Cs g-atom taken	Analysis of product			
									Cs %	F %	Cl %	Cs/F/Cl
1	2.58	1.33	0.52	0	42	1.5	1.08	183	—	[a]15.5	1.54	-/0.82/0.04
2	2.38	2.16	0.91	0	44	1.5	0.09	181	76.5	[c]19.7	0.73	1.0/1.8/0.04
3	1.86	1.93	1.04	0	66	1.5	trace	182	—	—	—	___
4	6.62	3.52	0.53	0	44	1.5	trace	170	78.2	[d]16.2	—	1.0/1.4/_
5	6.59	2.03	0.31	25	144	3	trace	175	77.4	[a]13.6	—	1.0/1.2/--
6	6.57	2.07	0.31	25	144	3	trace	179	—	—	—	___
7	6.52	3.03	0.46	0	144	1.5	trace	177	74.6	[b]20.7	0.58	1.0/1.9/0.03
8	3.49	1.17	0.34	25	64	3	0.46	172	76.2	[a]14.6	2.30	1.0/1.4/0.11
9	2.25	2.12	0.94	25	42	3	0.39	184	70.7	[b]19.3	trace	1.0/1.9/-
10	1.88	—	—	25	90	3	0.36	190	[d]81.5	[b]26.4	2.72	1.0/2.2/0.13
11	2.59	—	—	25	44	3	trace	177	75.4	[b]23.0	3.51	1.0/2.1/0.17
Ave.			0.59					179$\pm$5				

a). hydrolysis in open container
b). hydrolysis in closed system or on vacuum line
c). sample analyzed after fusion in quartz tube
d). high results due to incorrect sample weight

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TABLE II

X-Ray Data for CsF-ClO$_2$F Reaction Product.

d(Å)	I/Io	d(Å)	I/Io
4.18	MW	1.418	W
3.79	W	1.362	VW
3.39	W	1.345	VW
3.21-3.09	W	1.329	VW
2.99	W	1.283	VW
2.91	VW	1.241	VW
2.82	MS	1.217	VW
2.37	M	1.191	W
2.24	VW	1.144	W
2.17	VW	1.118	W
2.12	VW	1.079	MW
2.08	VVW	1.033	VVW
2.06	VVW	1.021	VW
1.91	MW	1.011	VW
1.86	W	0.997	VW
1.84	VW	0.967	VW
1.78	VW	0.944	VW
1.76	VW	0.923	VW
1.74	VW	0.907	VW
1.71	MW	0.884	VW
1.63	W	0.875	VW
1.52	VW	0.869	VW
1.481	VW		
1.439			

TABLE III

Data for Cs_2O-ClO_2F Reaction

Exp. No.	Cs_2O taken mmoles	ClO_2F consumed mmoles	$\dfrac{ClO_2F}{Cs_2O}$	reaction temperature °C.	reaction time hrs.	O_2 obtained mmoles	Cl_2 obtained mmoles	Ave. M.W. of product per Cs g-atom taken	Analysis of solid product			
									Cs	F	Cl	Cs/F/Cl
1	2.57	5.06	1.97	-78	7	3.54	1.98	170	70.4	10.3	5.67	1.0/1.0/0.3
2	1.68	4.02	2.39	25	1	4.31	1.40	152	82.1	5.80	4.67	1.0/0.5/0.2
3	1.92	3.63	1.89	25	64	3.70	0.84	168	72.3	3.21	7.82	1.0/0.3/0.4
4	1.90	2.03	1.07	-78	18	2.19	.55	159	76.6	6.43	4.69	1.0/0.6/0.2
5	1.79	3.80	———	flash at <78°		3.49	a 1.41	Wt. loss	-	-	-	1.0/0.6/0.2
6	1.67	3.44	———	flash at <78°		3.52	b 0.41	Wt. loss	-	-	-	1.0/1.2/0.6

a). 2.32 mmoles of $CClF_3$ also found.

b). 2.37 "   "   "   "

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TABLE IV

Data for PtF_6-ClF_3 Reaction

Exp. No.	PtF_6 taken mmoles	ClF_3 taken mmoles	$ClF_3 \cdot PtF_5$ obtained mmoles	$\dfrac{ClF_3 \cdot PtF_5}{ClF_3 \text{ taken}}$	ClF_5 obtained mmoles	$\dfrac{ClF_5}{ClF_3 \text{ taken}}$
1	2.67	2.67	1.80	0.67	____	____
2	2.67	2.67	2.68	1.00	1.22	0.46
3	2.98	2.98	2.55	0.86	0.84	0.28
4	3.10	3.10	2.57	0.83	1.59	0.51
5	3.39	3.39	2.57	0.76	1.22	0.36
6	3.43	5.16	3.24	0.63	1.96	0.38
7	3.50	5.27	3.34	0.63	1.99	0.38

TABLE V

Thermal Decomposition of $ClF_3 \cdot PtF_5$

Exp. No.	$ClF_3 \cdot PtF_5$ taken mmoles	Dec. Temp. °C.	ClF_3 obtained mmoles	F_2 obtained mmoles	PtF_4 obtained mmoles	$ClF_3 \cdot PtF_5/PtF_4/ClF_3/F_2$
1	2.43	520	2.49	_____	3.44	1.00/1.41/1.02/___
2	2.48	560	2.59	1.24	2.68	1.00/1.08/1.05/0.50
3	2.56	610	2.59	1.49	2.98	1.00/1.12/1.01/0.57
4	0.80	640	0.86	0.27	0.83	1.00/1.03/1.07/0.34

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